Electronic Supplementary Information

Anomaly in Stability of Hydroxides of Icosagens (B and Al) and Its Noble Gas (Xe and Rn) Derivatives: A Comparative Study

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Geometrical Parameters	Methods	HXeBO		HRnBO		HXeOAl		HRnOAl	
		Min	TS	Min	TS	Min	TS	Min	TS
R(H–Ng)	MP2/DEF2	1.799	1.585	1.889	1.673	1.680	1.582	1.783	1.670
	MP2/AVTZ	1.805	1.589	...[a]	...[a]	1.686	1.586	...[a]	...[a]
	B3LYP/DEF2	1.824	1.826	1.913	1.872	1.721	1.643	1.823	1.732
	B3LYP/AVTZ	1.826	1.831	...[a]	...[a]	1.724	1.646	...[a]	...[a]
R(Ng–B)/ R(Ng–O)	MP2/DEF2	2.487	3.207	2.549	3.249	2.193	2.563	2.263	2.614
	MP2/AVTZ	2.490	3.203	...[a]	...[a]	2.186	2.537	...[a]	...[a]
	B3LYP/DEF2	2.526	3.617	2.584	3.583	2.207	2.593	2.274	2.637
	B3LYP/AVTZ	2.527	3.620	...[a]	...[a]	2.204	2.586	...[a]	...[a]
R(B–O)/ R(O–Al)	MP2/DEF2	1.223	1.236	1.223	1.236	1.693	1.684	1.691	1.683
	MP2/AVTZ	1.224	1.238	...[a]	...[a]	1.702	1.693	...[a]	...[a]
	B3LYP/DEF2	1.208	1.214	1.208	1.215	1.681	1.669	1.679	1.669
	B3LYP/AVTZ	1.209	1.215	...[a]	...[a]	1.688	1.677	...[a]	...[a]
θ(H–Ng–B)/ θ(H–Ng–O)	MP2/DEF2	180	98.7	180	92.3	180	98.8	180	93.7
	MP2/AVTZ	180	98.7	...[a]	...[a]	180	98.8	...[a]	...[a]
	B3LYP/DEF2	180	86.2	180	82.5	180	102.3	180	97.2
	B3LYP/AVTZ	180	86.4	...[a]	...[a]	180	102.2	...[a]	...[a]
θ(Ng–B–O)/ θ(Ng–O–Al)	MP2/DEF2	180	177.9	180	178.8	180	179.2	180	178.6
	MP2/AVTZ	180	177.6	...[a]	...[a]	180	179.6	...[a]	...[a]
	B3LYP/DEF2	180	173.6	180	173.7	180	161.6	180	163.0
	B3LYP/AVTZ	180	172.8	...[a]	...[a]	180	161.7	...[a]	...[a]

[a]It is not possible to optimize the Rn containing molecules through GAMESS software due to the presence of h function in the AVTZ basis set.

Table S2. Optimized Structural Parameters (Bond Length R in Å, and Bond Angle θ in Degree) for the Minima Structures of HNgOB and HNgAlO (Ng = Xe and Rn) Molecules, Calculated using MP2 and B3LYP Methods with DEF2 and AVTZ Basis Sets and CCSD(T) Method with AVTZ Basis Set.

Geometrical Parameters	Methods	HXeOB	HRnOB	HXeAlO	HRnAlO
R(H–Ng)	MP2/DEF2	1.637	1.738	1.917	1.969
	MP2/AVTZ	1.642	...[a]	1.924	...[a]
	B3LYP/DEF2	1.682	1.779	1.911	1.980
	B3LYP/AVTZ	1.685	...[a]	1.913	...[a]
	CCSD(T)/AVTZ	1.656	1.758	...[b]	2.044
R(Ng–O)/ R(Ng–Al)	MP2/DEF2	2.340	2.411	2.945	2.990
	MP2/AVTZ	2.331	...[a]	2.951	...[a]
	B3LYP/DEF2	2.354	2.407	2.998	3.041
	B3LYP/AVTZ	2.349	...[a]	2.997	...[a]
	CCSD(T)/AVTZ	2.324	2.394	...[b]	3.066
R(O–B)/ R(Al–O)	MP2/DEF2	1.273	1.272	1.633	1.632
	MP2/AVTZ	1.276	...[a]	1.642	...[a]
	B3LYP/DEF2	1.260	1.259	1.610	1.610
	B3LYP/AVTZ	1.261	...[a]	1.618	...[a]
	CCSD(T)/AVTZ	1.275	1.273	...[b]	1.630
θ(H–Ng–O)/ θ(H–Ng–Al)	MP2/DEF2	176.6	175.3	180.0	180.0
	MP2/AVTZ	176.5	...[a]	180.0	...[a]
	B3LYP/DEF2	177.3	176.7	180.0	180.0
	B3LYP/AVTZ	177.3	...[a]	180.0	...[a]
	CCSD(T)/AVTZ	176.9	176.0	...[b]	180.0
θ(Ng–O–B)/ θ(Ng–Al–O)	MP2/DEF2	121.3	114.2	180.0	180.0
	MP2/AVTZ	121.1	...[a]	180.0	...[a]
	B3LYP/DEF2	130.9	127.2	180.0	180.0
	B3LYP/AVTZ	131.4	...[a]	180.0	...[a]
	CCSD(T)/AVTZ	123.8	118.4	...[b]	180.0

[a]It is not possible to optimize the Rn containing molecules through GAMESS software due to the presence of h function in the AVTZ basis set.

[b]It is not possible to optimize the HXeAlO molecule using CCSD(T)/AVTZ level of theory.

Table S3. Energies (in kJ mol^{-1}) of the Various Dissociated Species Relative to the HNgBO and HNgOAl (Ng = Xe and Rn) Molecules, Calculated using MP2 and B3LYP Methods with DEF2 and AVTZ Basis Sets.

Molecular Species	Methods	HXeBO	HRnBO	HXeOAl	HRnOAl
HNgBO/HNgOAl	**All**	0.0	0.0	0.0	0.0
Ng + HBO/HOAl	**MP2/DEF2**	−457.5	−417.7	−411.7	−378.9
	MP2/AVTZ	−453.9	...[a]	−403.6	...[a]
	B3LYP/DEF2	−437.9	−401.1	−411.4	−378.9
	B3LYP/AVTZ	−437.4	...[a]	−408.4	...[a]
HNg + BO/OAl	**MP2/DEF2**	16.7	56.6	140.9	173.8
	MP2/AVTZ	20.5	...[a]	151.9	...[a]
	B3LYP/DEF2	51.0	87.7	77.7	110.3
	B3LYP/AVTZ	51.0	...[a]	76.3	...[a]
$HNg^+ + BO^-/OAl^-$	**MP2/DEF2**	594.6	609.4	615.1	622.9
	MP2/AVTZ	597.8	...[a]	624.8	...[a]
	B3LYP/DEF2	610.9	621.5	637.5	643.9
	B3LYP/AVTZ	611.4	...[a]	641.7	...[a]
H + Ng + BO/OAl	**MP2/DEF2**	17.0	56.8	141.3	174.0
	MP2/AVTZ	20.8	...[a]	152.2	...[a]
	B3LYP/DEF2	51.0	87.8	77.7	110.3
	B3LYP/AVTZ	51.0	...[a]	76.2	...[a]
$H^+ + Ng + BO^-/OAl^-$	**MP2/DEF2**	1102.1	1141.9	1122.6	1155.4
	MP2/AVTZ	1102.5	...[a]	1129.5	...[a]
	B3LYP/DEF2	1120.6	1157.4	1147.2	1179.8
	B3LYP/AVTZ	1120.0	...[a]	1150.2	...[a]
Barrier Height[b]	**MP2/DEF2**	208.1	222.5	164.0	174.0
	MP2/AVTZ	209.0	...[a]	168.1	...[a]
	B3LYP/DEF2	200.6	211.9	172.9	182.8
	B3LYP/AVTZ	200.6	...[a]	175.8	...[a]

[a]It is not possible to optimize the Rn containing molecules through GAMESS software due to the presence of h function in the AVTZ basis set.

[b]Barrier Height corresponding to TS (Transition State), (HNgBO → HBO + Ng; HNgOAl → HOAl + Ng).

Table S4. Energies (in kJ mol^{-1}) of the Various Dissociated Species Relative to the HNgOB and HNgAlO (Ng = Xe and Rn) Molecules, Calculated using MP2 and B3LYP Methods with DEF2 and AVTZ Basis Sets and CCSD(T) Method with AVTZ Basis Set.

Molecular Species	Methods	HXeOB	HRnOB	HXeAlO	HRnAlO
HNgOB/HNgAlO	**All**	0.0	0.0	0.0	0.0
Ng + HOB/HAlO	**MP2/DEF2**	−337.3	−301.1	−369.2	−331.6
	MP2/AVTZ	−332.7	...[a]	−364.2	...[a]
	B3LYP/DEF2	−333.4	−298.2	−342.0	−307.5
	B3LYP/AVTZ	−332.1	...[a]	−342.3	...[a]
	CCSD(T)/AVTZ	−339.3	−301.8	...[b]	−308.4
HNg + OB/AlO	**MP2/DEF2**	−73.5	−37.2	35.2	72.8
	MP2/AVTZ	−66.9	...[a]	42.0	...[a]
	B3LYP/DEF2	−41.4	−6.2	−26.9	7.5
	B3LYP/AVTZ	−40.0	...[a]	−32.0	...[a]
	CCSD(T)/AVTZ	−41.6	−4.2	...[b]	11.0
$HNg^+ + OB^-/AlO^-$	**MP2/DEF2**	504.5	515.7	509.3	522.0
	MP2/AVTZ	510.4	...[a]	514.9	...[a]
	B3LYP/DEF2	518.5	527.5	532.8	541.2
	B3LYP/AVTZ	520.4	...[a]	533.5	...[a]
	CCSD(T)/AVTZ	515.5	526.6	...[b]	531.2
H + Ng + OB/AlO	**MP2/DEF2**	−73.2	−36.9	35.5	73.1
	MP2/AVTZ	−66.6	...[a]	42.3	...[a]
	B3LYP/DEF2	−41.4	−6.2	−26.9	7.6
	B3LYP/AVTZ	−40.0	...[a]	−32.0	...[a]
	CCSD(T)/AVTZ	−41.0	−3.6	...[b]	11.6
$H^+ + Ng + OB^-/AlO^-$	**MP2/DEF2**	1012.0	1048.2	1016.8	1054.5
	MP2/AVTZ	1015.1	...[a]	1019.6	...[a]
	B3LYP/DEF2	1028.2	1063.4	1042.5	1077.1
	B3LYP/AVTZ	1028.9	...[a]	1042.0	...[a]
	CCSD(T)/AVTZ	1031.5	1068.9	...[b]	1073.4

[a]It is not possible to optimize the Rn containing molecules through GAMESS software due to the presence of h function in the AVTZ basis set.

[b]It has not been possible to optimize the geometry of HXeAlO by employing CCSD(T) method with AVTZ basis set.

Table S5. MP2 and B3LYP Calculated Values of the Partial Mulliken Charges in HNgBO and HNgOAl (Ng = Xe and Rn) Molecules using DEF2 and AVTZ Basis Set.

Charges	Methods	HXeBO		HRnBO		HXeOAl		HRnOAl	
		Min	TS[a]	Min	TS[a]	Min	TS[a]	Min	TS[a]
q(H)	MP2/DEF2	−0.159	0.179	−0.206	0.138	−0.020	0.160	−0.071	0.122
	MP2/AVTZ	−0.223	0.008	...[b]	...[b]	−0.189	−0.025	...[b]	...[b]
	B3LYP/DEF2	−0.123	0.070	−0.177	0.036	−0.018	0.122	−0.066	0.084
	B3LYP/AVTZ	−0.179	−0.073	...[b]	...[b]	−0.149	−0.007	...[b]	...[b]
q(Ng)	MP2/DEF2	0.506	0.720	0.538	0.761	0.637	0.697	0.694	0.732
	MP2/AVTZ	0.663	0.886	...[b]	...[b]	0.913	0.892	...[b]	...[b]
	B3LYP/DEF2	0.428	0.443	0.478	0.508	0.618	0.580	0.654	0.621
	B3LYP/AVTZ	0.613	0.554	...[b]	...[b]	0.818	0.766	...[b]	...[b]
q(O)	MP2/DEF2	−0.345	−0.434	−0.399	−0.384	−0.307	−0.484	−0.314	−0.475
	MP2/AVTZ	−0.308	−0.423	...[b]	...[b]	−0.622	−0.683	...[b]	...[b]
	B3LYP/DEF2	−0.310	−0.315	−0.369	−0.300	−0.239	−0.402	−0.222	−0.388
	B3LYP/AVTZ	−0.420	−0.398	...[b]	...[b]	−0.685	−0.725	...[b]	...[b]
q(B)/*q*(Al)	MP2/DEF2	−0.002	−0.465	0.067	−0.515	−0.311	−0.374	−0.310	−0.379
	MP2/AVTZ	−0.132	−0.471	...[b]	...[b]	−0.102	−0.184	...[b]	...[b]
	B3LYP/DEF2	0.005	−0.197	0.068	−0.244	−0.360	−0.300	−0.366	−0.317
	B3LYP/AVTZ	−0.014	−0.084	...[b]	...[b]	0.016	−0.035	...[b]	...[b]

[a]Transition state

[b]It is not possible to optimize the Rn containing molecules through GAMESS software due to the presence of h function in the AVTZ basis set.

Table S6. Harmonic Vibrational Frequencies (in cm^{-1}) Calculated using MP2 [B3LYP] Methods with DEF2 and AVTZ Basis Sets for HNgBO and HNgOAl (Ng = Xe and Rn) Molecules for the Minima and the Transition States (TS). Corresponding IR Intensity Values Calculated using B3LYP and MP2 Methods are given within the Parentheses (in km mol^{-1}).

Normal Modes	Basis Set	HXeBO		HRnBO		HXeOAl		HRnOAl	
		Min	TS	Min	TS	Min	TS	Min	TS
H–Ng Stretch	DEF2	1510.3 (1615.5) [1468.4] (1289.2)	1757.1 (46.9) [1050.0] (3933.8)	1536.2 (1393.9) [1478.4] (1153.7)	1759.0 (57.2) [1162.5] (3575.8)	1941.0 (1365.9) [1756.6] (1819.2)	2429.0 (101.4) [1744.4] (16.6)	1850.7 (1328.0) [1690.5] (1700.5)	2285.4 (71.4) [1639.2] (9542.8)
	AVTZ	1496.3 (1585.7) [1470.5] (1291.7)	1755.3 (47.5) [1040.7] (4012.4)	...[b]	...[b]	1922.5 (1362.2) [1753.3] (1817.5)	2419.7 (83.9) [1742.7] (8751.6)	...[b]	...[b]
Ng–B/ Ng–O Stretch	DEF2	253.3 (89.3) [234.1] (77.8)	167.7 (52.9) [95.2] (1.0)	253.3 (80.8) [235.9] (69.0)	161.7 (52.7) [99.5] (1.8)	275.3 (67.8) [264.3] (41.8)	196.0 (79.6) [176.9] (3.5)	265.5 (58.4) [256.3] (36.5)	185.4 (72.8) [168.2] (2.7)
	AVTZ	252.0 (87.8) [234.6] (77.8)	168.7 (52.5) [94.2] (1.5)	...[b]	...[b]	281.9 (61.9) [268.7] (40.4)	201.6 (81.4) [177.8] (1.6)	...[b]	...[b]
B–O/ O–Al Stretch	DEF2	1846.9 (22.7) [1912.6] (71.0)	2390.5 (151.1) [1843.3] (180.0)	1849.1 (30.5) [1914.6] (81.1)	2247.9 (131.7) [1843.0] (174.1)	894.9 (736.0) [889.0] (519.5)	885.6 (408.3) [874.4] (0.2)	902.2 (717.9) [898.3] (507.7)	888.7 (395.1) [873.1] (6.5)
	AVTZ	1843.6 (23.4) [1913.0] (70.4)	2379.2 (139.5) [1843.4] (183.2)	...[b]	...[b]	892.6 (752.3) [885.9] (529.2)	876.6 (432.7) [868.3] (1.4)	...[b]	...[b]

H–Ng–B/ H–Ng–O Bend[a]	**DEF2**	634.1 (0.6) [598.6] (0.3)	–649.8 (6.6) [–504.0] (1.7)	569.4 (2.2) [536.2] (1.5)	–571.4 (17.6) [–515.8] (2.7)	638.7 (1.5) [601.8] (2.9)	–580.2 (9.2) [–732.6] (2012.6)	560.3 (3.9) [525.7] (5.4)	–539.1 (1.1) [–724.9] (2412.1)
	AVTZ	627.7 (35.1) [599.7] (34.6)	–651.9 (14.0) [–500.8] (25.0)	…[b]	…[b]	633.9 (41.2) [605.3] (42.6)	–591.8 (54.7) [–735.8] (2061.9)	…[b]	…[b]
Ng–B–O/ Ng–O–Al Bend[a]	**DEF2**	152.9 (5.8) [154.0] (7.8)	89.4 (9.5) [64.1] (0.6)	162.3 (7.1) [161.1] (9.4)	88.6 (8.5) [68.3] (0.6)	55.1 (8.4) [76.6] (8.5)	52.0 (7.2) [105.2] (19.6)	53.2 (6.2) [77.1] (6.5)	51.8 (5.5) [97.0] (13.9)
	AVTZ	148.6 (10.3) [152.9] (12.0)	88.9 (8.8) [58.4] (1.3)	…[b]	…[b]	69.4 (9.8) [64.4] (10.0)	59.5 (12.6) [78.2] (22.6)	…[b]	…[b]
H–Ng–B–O/ H–Ng–O–Al Torsion	**DEF2**	…[c]	84.2 (13.5) [51.4] (0.0)	…[c]	83.7 (9.5) [57.3] (0.003)	…[c]	49.0 (8.3) [86.8] (23.6)	…[c]	48.8 (7.0) [85.8] (21.7)
	AVTZ	…[c]	81.6 (22.3) [50.9] (0.01)	…[c]	…[b]	…[c]	56.9 (7.7) [76.5] (18.9)	…[c]	…[b]

[a]The modes are doubly degenerate for minima.

[b]It is not possible to optimize the Rn containing molecules through GAMESS software due to the presence of h function in the AVTZ basis set.

[c]There is no torsional modes of vibration for the minima structures.

Table S7. MP2 [B3LYP] Calculated Values of the Harmonic Vibrational Frequencies (in cm^{-1}) and Intrinsic Force Constants in Parentheses (in N m^{-1}) Corresponding to Individual Internal Coordinates for the Minima Structure of HNgBO and HNgOAl (Ng = Xe and Rn) Molecules, Calculated using DEF2 and AVTZ Basis Sets.

Normal Modes	Basis Set	HXeBO	HRnBO	HXeOAl	HRnOAl
H–Ng Stretch	DEF2	1510.5 (134.5) [1468.4] (127.0)	1536.1 (139.5) [1478.1] (129.1)	1940.5 (221.9) [1756.5] (181.8)	1849.5 (202.2) [1690.1] (168.8)
	AVTZ	1496.4 (131.9) [1470.5] (127.4)	...[a]	1922.0 (217.7) [1753.2] (181.1)	...[a]
Ng–B/ Ng–O Stretch	DEF2	396.4 (94.0) [371.3] (82.5)	405.1 (101.4) [380.5] (89.5)	422.4 (149.9) [384.8] (124.5)	423.9 (158.0) [389.4] (133.3)
	AVTZ	393.6 (92.7) [372.3] (83.0)	...[a]	438.0 (161.3) [396.0] (131.8)	...[a]
B–O/ O–Al Stretch	DEF2	1821.5 (1274.6) [1890.8] (1373.5)	1821.9 (1275.3) [1891.3] (1374.4)	836.7 (414.2) [844.0] (421.5)	842.0 (419.4) [850.0] (427.5)
	AVTZ	1818.5 (1270.6) [1891.0] (1373.8)	...[a]	828.4 (406.0) [837.0] (414.5)	...[a]
H–Ng–B/ H–Ng–O Bend	DEF2	620.8 [585.2]	555.9 [522.6]	639.1 [602.1]	560.7 [526.0]
	AVTZ	614.1 [586.4]	...[a]	634.2 [605.5]	...[a]
Ng–B–O/ Ng–O–Al Bend	DEF2	200.3 [198.8]	203.7 [201.0]	49.9 [74.5]	48.7 [75.6]
	AVTZ	197.3 [197.9]	...[a]	66.0 [62.3]	...[a]

[a]It is not possible to optimize the Rn containing molecules through GAMESS software due to the presence of h function in the AVTZ basis set.